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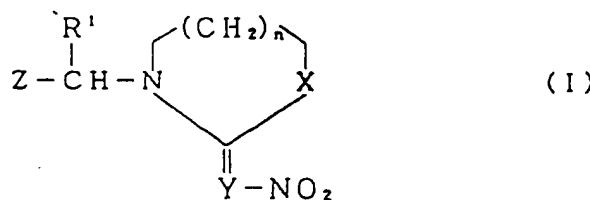
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㉒ Agents for preserving technical materials against insects.

㉓ The use of the compounds of the formula (I)



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as agents for preserving technical materials against insects.

The present invention relates to the use of known nitromethylene or nitroimino compounds as agents for combating technical materials destroying insects in order to preserve these materials.

The present invention also relates to compositions useful for combating these insects, preserving technical materials completely, i.e. not only against insects but also against fungi, bacteriae and algae and for treating soil to protect technical materials against termite infestations.

5 The invention furthermore relates to processes for treating technical materials and for soil treatment against termite infestations.

The compounds and their insecticidal use in the field of plant protection has already been known. Compare for example with EP-A 163855 and EP-A 192060.

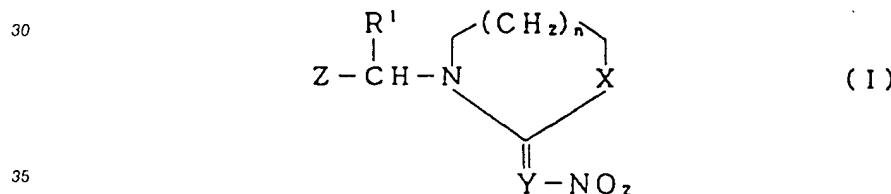
10 Insecticidal agents and compositions of said compounds and their use to preserve technical materials completely and to treat soil against-termite infestations have not been known up to now.

Different insects are known as pests infesting technical materials so that due to serious damages caused thereby undesirable effects on living environment and cultural assets principally made of these materials have posed a social problem, urgently requiring effective controlling of the pests. Termites are 15 known as important examples of these pests.

At present, use for combating technical materials destroying insects has been made of organophosphorus insecticides such as phoxim [0-(α -cyanobenzylideneamino)0,0-diethylphosphorothioate], chloropyriphos [0,0-diethyl-3,5,6-trichloro-2-pyridylphosphorothioate], etc., as well as pyrethroides series insecticides such as permethrin [5-benzyl-3-furylmethyl-3-(2-methoxy-carbonyl-1-propenyl)-2,2-dimethyl-20 cyclopropane carboxylate], decamethrin [α -cyano-3-phenoxybenzyl d,l-cis-3-(2,2-dibromovinyl)-2,2-dimethyl cyclopropane carboxylate], cypermethrin [α -cyano-3-phenoxybenzyl (\pm) cis, trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], fenvalerate [(RS)- α -cyano-3-phenoxybenzyl (RS)-2-(4-chlorophenyl)-3-methylbutyrate], cyflutrine [cyano-(4-fluoro-3-phenoxyphenyl) methyl-3-(2,2-dichloroethenyl)-2,2-dimethyl-cyclopropane carboxylate].

25 However, the above-mentioned insecticides are unsatisfactory as far as effective concentration and the long lasting effect are concerned.

It has been found that the known compounds of the formula (I)



wherein X is NH or S,

Y is CH or N

40 Z is 2-chloro-5-pyridyl or 2-chloro-5-thiazolyl,

R¹ is hydrogen or methyl, and

n is 0 or 1,

exhibit powerful insecticidal properties on material destroying insects and preferably on termites.

The compounds according to the invention of the formula (I) surprisingly exhibit an extremely strong 45 insecticidal action on material destroying insects and the function is substantially superior to that of known insecticidal agents.

The compounds of the formula (I) can be used to preserve technical materials against insects.

In the formula (I), the individual residues have the following preferable meanings:

X is NH or S,

50 Y is CH or N,

Z is 2-chloro-5-pyridyl,

R¹ is hydrogen, and

n is 0 or 1.

As examples of the active substances to be used according to the invention, the following ones are 55 particularly preferred:

1-(6-chloro-3-pyridylmethyl)-2-nitromethyleneimidazolidine,

3-(6-chloro-3-pyridylmethyl)-2-nitromethylenethiazolidine,

1-(6-chloro-3-pyridylmethyl)-2-nitroiminoimidazolidine,

1-(6-chloro-3-pyridylmethyl)-2-nitromethylenetetrahydropyrimidine, and
3-(6-chloro-3-pyridylmethyl)-2-nitromethylenetetrahydro-2H-1,3-thiazine.

The active substances to be used according to the invention exhibit powerful insecticidal effects against material destroying insects.

5 They can therefore be used in insecticidal agents for combating material destroying insects and preserving technical materials. They can also be used for soil treatment against termite infestation.

As individual examples of technical materials preserved by means of the insecticidal agents according to the present invention the following ones can be mentioned: wood or composite wood-materials (such as pressed wood, particle board, chip board, wafer board, plywood, wood laminated material, freshly cut 10 timber/lumber etc.), paper, leather or leather products, natural or synthetic polymers, textiles.

Preferable materials are wood or composite wood-materials.

As individual examples of insects to be combated or controled by the active substances of formula (I) according to the present invention the following ones can be mentioned:

15 Order Isoptera

Mastotermitidae

Kalotermitidae such as Kalotermes spp.
Cryptotermes spp. etc.

20 Termopsidae such as Zootermopsis spp. etc.

Rhinotermitidae

such as Reticulitermes spp.
Heterotermes spp.

25 Termitidae such as Amitermes spp.
Nasutitermes spp.

Acanthotermes spp.
Mikrotermes spp. etc.

30 Order Coleoptera

Lyctidae

such as Lyctus brunneus etc.

Bostrychidae

such as Bostrychus capucinus
Dinoderus minutus etc.

35 Anobiidae such as Anobium punctatum

Xyletinus peltatus
Xestobium rufovillosum
Ptilinus pectinicornis etc.

Cerambycidae

such as Hylotrupes bajulus
Hesperophanus cinereus
Stromatium fulvum
Chlorophorus pilosus etc.

Oedemeridae

Serropulidae

45 Curculionidae

Seolytida

Platypodidae

Order Hymenoptera

50

Siricidae such as Sirex spp.

Urocerus spp.

Formicidae such as Camponotus spp.

In the above Isopteroes insects, especially, there may be mentioned as examples of termites in Japan:

55 Deucotermes speratus,

Coptotermes formosanus,

Glyptotermes fucus,

Glyptotermes satsumensis,

Glyptotermes nakajimai,
 Glyptotermes Kodamai,
 Incisitermes minor,
 Neotermes koshunensis,
 5 Cryptotermes domesticus,
 Hodotermopsis japonica,
 Reticulitermes miyatakei,
 Odontotermes formosanus,
 Nasutitermes takasagoensis,
 10 Capritermes nitobei and so on.

The active compounds of the general formula (I) in the present invention can be prepared into the customary formulations, such as solutions, emulsions, suspensions, powders, foams, pastes, granules, aerosols, natural and synthetic materials impregnated with active compounds, and micro-capsules.

These formulations may be produced in a known manner, for example, by mixing the active compounds with extenders, that is to say liquid or liquefied gaseous or solid diluents or carriers, optionally with the use of surface-active agents, that is to say emulsifying agents, dispersing agents, and/or foam-forming agents. In the case of using water as an extender, organic solvents can, for example, also be used as auxiliary solvents.

As liquid diluents or carriers can be mentioned, for example, aromatic hydrocarbons, such as xylene, toluene and alkyl naphthalenes, chlorinated aromatic or chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes and methylene chloride, aliphatic or alicyclic hydrocarbons, such as cyclohexane or paraffins, for example, mineral oil fractions, alcohols, such as butanol or glycol as well as their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, or strongly polar solvents, such as dimethylformamide and dimethylsulfoxide, as well as water.

By liquefied gaseous diluents or carriers are meant liquids which are gaseous at normal temperature and under normal pressure, for example, aerosol propellants, such as halogenated hydrocarbons as well as butane, propane, nitrogen and carbon dioxide.

As solid diluents there may be used ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as highly-dispersed silicic acid, alumina and silicates.

As solid carriers for granules there may be used crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, as well as synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks.

As emulsifying and/or foam-forming agents there may be used nonionic and ionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example, alkylaryl polyglycol ethers, alkylsulfonates, alkylsulfates, arylsulfonates as well as albumin hydrolysis products. Dispersing agents include, for example, lignin sulfite waste liquors and methyl cellulose.

Adhesives such as carboxymethyl cellulose and natural and synthetic polymers, (such as gum arabic, polyvinyl alcohol and polyvinyl acetate) can be used in the formulations in the form of powders, granules or emulsifiable concentrations.

It is possible to use colorants such as inorganic pigments, for example, iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs or metal phthalocyanine dyestuffs, and trace elements, such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations, in general, contain from 0.001 to 95 percent by weight of active compound, preferably from 0.5 to 90 percent by weight.

Furthermore, the active compound of the present invention having the formula (I) can be present as a mixture with a synergist in a formulation or a use form, of the type that is commercially useful. The term "synergist" denotes a compound which is not active in itself, but promotes the action of an active compound. The content of the active compounds having the general formula (I) of the present invention in commercially useful formulations can vary within a wide range. The active compound concentration of the formulation for use is, for example, from 0.0000001 to 100 percent by weight, preferably from 0.0001 to 1 percent by weight.

In order to protect the above-mentioned materials completely, i.e. not only against material destroying insects but also against fungi, bacteria and algae, they can be treated with compositions containing at least one insecticidally active compound of the formula (I) and at least one biological active fungicide, bactericide or algicide.

Wood or composite wood-materials can preferably be treated with a composition containing
 a) an insecticidally effective amount of a compound of the formula (I) or mixtures thereof and
 b) a fungicidally effective amount of at least one compound selected from the group of
 Trihalosulphenyl-Compounds such as

5 - N-Dichlorofluoromethylthio-N',N'-dimethyl-N-phenylsulfuric acid diamide (Dichlofluanide)
 - N-Dichlorofluoromethylthio-N',N'-dimethyl-N-p-tolylsulphamide (Tolylfluanide)
 - N-Trichloromethylthiophthalimide (Folpet)
 - N-Dichlorofluoromethylthiophthalimide (Fluorfolpet) etc.

Iodine-Compounds such as

10 - 3-Iodo-2-propynyl-butylcarbamate (IPBC)
 - 3-Iodo-2-propynyl-hexylcarbamate
 - 3-Iodo-2-propynyl-cyclohexylcarbamate
 - 3-Iodo-2-propynyl-phenylcarbamate
 - Diiodmethyl-p-tolylsulphone (Amical 48) etc.

15 Phenols such as

- ortho-Phenylphenol
- Tribromophenol
- Tetrachlorophenol
- Pentachlorophenol etc.

20 Azole-Compounds such as

- 1-(4-Chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4 triazol-1-yl)-2-butanone (Triadimefon)
- β -(4-Chlorophenoxy)- α -(1,1 dimethyl-ethyl)-1H-1,2,4 triazole-1-ethanol (Triadimenol)
- $\pm\alpha$ [2-(4-chlorophenyl) ethyl]- α -(1,1-dimethylethyl)-1H-1,2,4-triazole-1-ethanol (Tebuconazole)
- 1-[2(2,4-dichlorophenyl) 4-propyl-1,3-dioxolan-2-ylmethyl]-1H-1,2,4-triazole (Propiconazol)
- 1-[2(2,4-dichlorophenyl)-1,3-dioxolan-2-ylmethyl]-1H-1,2,4-triazole (Azaconazol)
- (RS)-2(2,4-dichlorophenyl)-1-(1H-1,2,4 triazol-2-yl)-2-ol (Hexaconazol)
- 1-N-propyl-N-[2-(2,4,6-trichlorophenoxy) ethyl] carbamoylimidazol (Prochloraz) etc.

Tin Compounds such as

30 - Tributyl tin octoate
 - Tributyl tin oleate
 - Bistributyl tin oxide
 - Tributyl tin naphthenate
 - Tributyl tin phosphate
 - Tributyl tin benzoate etc.

35 Thiocyanate Compounds such as

- Methylenebisthiocyanate (MBT)
- 2-Thiocyanomethylthiobenzothiazole (TCMTB) etc.

Quarternary Ammonium Compounds such as

40 - Benzyl-dimethyl-tetradecylammoniumchloride
 - Benzyl-dimethyl-dodecylammoniumchloride etc.

Benzimidazole Compounds such as

45 - 2-(2'-Furyl)-1H-benzimidazole (Fuberidazole)
 - Methylbenzimidazol-2-ylcarbamate (BCM)
 - 2-(4'-thiazolyl) benzimidazole (Thiabendazole)
 - Methyl (1-butylcarbamoyl)-2-benzimidazole carbamate (Benomyl)

Isothiazolinone Compounds such as

50 - N-Methylisothiazolin-3-one
 - 5-Chloro-N-methylisothiazolin-3-one
 - 4,5-Dichloro-N-octylisothiazolin-3-one
 - N-Octylisothiazolin-3-one

Morpholine Compounds such as

55 - $C_{14}-C_{11}$ -4-Alkyl-2,6-dimethylmorpholine (Tridemorph)

Pyridine Compounds such as

55 - 1-Hydroxy-2-pyridine-thione and Sodium Iron, Manganese or Zinc-Salt thereof
 - Tetrachloro-4-methyl sulphonyl pyridine

N-Cyclohexyldiaziniumdioxy Compounds such as

- Tris-(N-cyclohexyldiaziniumdioxy) aluminium
- Bis-(N-cyclohexyldiaziniumdioxy) copper

Naphthenate Compounds such as

- Zincnaphthenate

Quinoline Compounds such as the copper salt of

- 8-hydroxy-quinoline

5 Nitriles such as

- 1,2,3,5-Tetrachloro-4,6-cyanobenzene.

Boric compounds such as boric acid, borax, boratesUreas such as N¹(3,4-dichlorophenyl)-N,N-dimethylureaFurane derivatives such as Furmecyclo

10 These fungicidally effective compounds are added to the composition in order to prevent wood or wood materials not only against wood destroying insects but also against

- Wood-discoloring fungi such as

Ascomycetes (Caratocystis minor)15 Deuteromycetes (Aspergillus niger, Aureobasidium pullulans, Dactyleum fusarioides, Penicillium Variabile, Sclerophoma pithyophila, Scopularia phycomyces, Trichoderma viride, Trichoderma liigororum)Zygomycetes (Mucor spinosus)

and/or

- Wood-destroying fungi such as

20 Ascomycets (Chetomium alba-arenulum, Chaetonium globosum, Humicola grisea, Petriella setifera, Trichurus spiralis)Basidiomycetes(Coniophera puteanaCoriolus versicolor25 Donbiopora expansaGlenospora graphiiGloeophyllum abietinumGloeophyllum adoratumGloeophyllum protactum30 Gloeophyllum trabeumGloeophyllum sepiariumLentinus cyathioformesLentinus edodesLentinus lepideus35 Lentinus squarvolosusPaxillus panuoidesPleurofus ostreatusPoria placentaPoria monticola40 Poria vaillantiiPoria vaporiaSerpula himantoidesSerpula lacrymansTyromyces palustris)45 Deuteromycetes (Cladosporium herbarum).

Generally the compositions also will include at least one additional diluent, emulsifier, melting agent, organic binding agent, auxiliary solvents, processing additives, fixatives, plasticizers, UV-stabilizers or stability enhancers, dyes (water soluble, water insoluble), color pigments, siccatives, corrosion inhibitors, antisettlement agents, additional insecticides (such as insecticidal carbamates, organophosphorus compounds, halogenated hydrocarbons, pyrethroides etc.), anti skinning agents and the like.

The above-mentioned additional ingredients and their use are described in prior art. (EP-A 0370665, DE-A 3531257, DE-A 3414244).

The compositions according to the present invention generally comprise from about 10^{-6} to 30 parts by weight, preferably from about 0.0005 to 15 parts by weight and more preferably from 0.005 to 2 parts by weight of the insecticide of formula (I) and from 0.01 to 90 parts by weight, preferably from about 0.05 to 50 parts by weight and more preferably from 0.1 to 30 parts by weight of at least one of the above-mentioned fungicides.

The compositions can be provided as ready for use products or as concentrates, which have to be

diluted prior to use.

The compositions can be applied by means of brushing, spraying, dipping, double vacuum and the like as known in the art. The compositions can be prepared by any technique known in the art.

The content of the present invention will be concretely explained by way of the following examples but the present invention should not be limited only thereto.

Examples for compositions:

*Remark: the percentages are given in percent by weight

10

Example 1

15

0.005%	1-(6-chloro-3-pyridylmethyl)-2-nitroiminoimidazolidine (imidacloprid)
5 %	Butylglycol
94.995%	Mineral spirits

20

Example 2 Impregnating agent/Primer

25

0.01 %	Imidacloprid
0.5 %	Dichlofluanide
1. %	Tebuconazole
9.7 %	Alkyd resin (solid)
88.79 %	Mineral spirits

30

Example 3 Wood stain/low build

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0.01 %	imidacloprid
0.5 %	Dichlofluanide
1.2 %	Tebuconazole
21 %	Alkyd resin (solid)
2 %	Pigment
4 %	Antisettlement additive, dryes etc.
71.29%	Mineral spirits

Example 4 Wood stain/high build

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0.015%	imidacloprid
0.6 %	Dichlofluanide
1.5 %	Tebuconazole
40 %	Alkyd resin
2 %	Pigment
4 %	Antisettlement additive, dryer etc.
48.115%	Mineral spirits

55

Example 5 Soil treatment

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20 %	imidacloprid
8 %	ethylene glycol
3 %	emulsifiers
0.25 %	thickeners
68.75 %	distilled water

Example 6 Wood brushing

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15

0.1 %	imidacloprid
1 %	3-bromo-2,3-diiodo-2-propenyl ethylcarbonate
98.9 %	organic solvents

25

Example 7 wood brushing

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0.1 %	imidacloprid
1.5 %	4-chlorophenyl-3-iodopropargylformal
98.4 %	organic solvents

Example 8 Formicidal test

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Compounds under test

Examples of the active compounds according to the present invention

- I.1: 1-(6-chloro-3-pyridylmethyl)-2-nitromethyleneimidazolidine
- I.2: 3-(6-chloro-3-pyridylmethyl)-2-nitromethylenethiazolidine
- I.3: imidacloprid

35 Comparative compounds

A : phoxim
B : chloryrifos

40 Preparation of test formulation:

Solvent: 3 parts by weight of xylene
Emulsifier: 1 part by weight of polyoxyethylene-alkylphenyl-ether
To prepare a suitable formulation of the active compound, 1 part by weight of each of the active compounds was mixed with the above-mentioned amount of the solvent containing the above-mentioned amount of the emulsifier, and the mixture was diluted with water to a predetermined concentration.

45 Test method:

50 1 ml of the aqueous solution prepared in the above-mentioned procedure was uniformly applied using a pipette onto a filter paper that was placed in petri dish of 9 cm diameter. Ten head of worker termites (*Coptotermes formosanus*) were replaced into the petri dish and it was kept in a constant temperature chamber at 25 °C.
After four days, the mortality of the termites was investigated. This test procedure was carried out in 55 duplicate per each concentration of the active compounds under test.
The test results are shown in Table 1.

Table 1

Compound	Concentration of active compound (ppm)	Mortality of termites after four days (%)
I.1	40	100
	8	100
	1.6	100
	0.32	100
I.2	40	100
	8	100
	1.6	100
	0.32	100
I.3	40	100
	8	100
	1.6	100
	0.32	100
A	40	100
	8	100
	1.6	100
	0.32	90
B	40	100
	8	100
	1.6	100
	0.32	100
Untreated		0

Example 9 Test on Residual Effect

Small blocks of Japanese redpine tree (2 cm x 2 cm x 2 cm) were soaked for one minute into the aqueous solution prepared by the similar procedure to Example 8.

After air-dried, they were kept in a constant temperature chamber at 40°C for four weeks. Then each of the thus treated blocks was placed in a polymeric cup (10 cm diameter) containing 150 ml of sandy loam of 20 % moisture content. Into each of the polymeric cups, 100 head of working termites and 10 head of soldier termites (Coptotermes formosanus) were released. After three weeks, the degree of xylophagous damage in the block and the mortality of the termites were investigated.

Three tests were carried out in duplicate 25°C, and the results are shown in Table 2.

The index of xylophagous damage observed on the test blocks:

- 0 : No damage
- 0.5 : One to two traces of damage each having a depth of about 1 mm from the block surface
- 1 : One to two evident damages each having a depth from 1 to 2 mm from the block surface
- 2 : More than three evident damages or more than one deep trace of damage having a depth of more than 2 mm from the block surface
- 3 : More than three deep damages
- 4 : Evidently damaged zone covering up to about one third of the whole surface area of the block
- 5 : Evidently damaged zone covering more than one third of the whole surface area of the block

Table 2

Compound	Concentration of active compound (ppm)	Mortality termites after three weeks (%)	Degree of xylophagous damage in the pine tree block (0 - 5)
I.1	40	100	0
	8	100	0
	1.6	100	0
	0.32	98	0.5
I.2	40	100	0
	8	100	0
	1.6	100	0
	0.32	100	0
I.3	40	100	0
	8	100	0
	1.6	100	0
	0.32	100	0
A	40	25	3
	8	0	5
	1.6	0	5
	0.32	0	5
B	40	100	0
	8	78	1
	1.6	0	3
	0.32	0	5
Untreated		0	5

Example 10 Toxic value against larvae of *Hylotrupes bajulus*

The toxicity against larvae of *Hylotrupes bajulus*, using wood samples treated with the active compound I.3 provided in Example 8 in chloroform having concentrations of 1.44×10^{-5} %, 1.44×10^{-4} %, 7.2×10^{-3} %, and 1.44×10^{-2} % was determined according to the detailed description of DIN EN 47 (edition 1990, Beuth Verlag GMBH) which is concerned with the European standard method prescribed by the European Committee for standardization concerning wood preservatives, determination of the toxic value against larvae of *Hylotrupes bajulus*.

An outline of the method is as follows: (see DIN EN 47 for detail)

Five wood-samples (50 mm x 25 mm x 15 mm) which are treated by the active compound beforehand (impregnation treatment in vacuum) are provided and in each specimen, a regular pattern of six holes are bored, and then one head of the larvae is inserted per a hole.

After four weeks, the specimens are cut up in turn and the number of live/dead of larvae is determined.

In determination, where a live larvae is identified in a specimen, then the remaining specimens without cutting up are stored for a further eight weeks, and afterward, the number of live/dead larvae is determined.

From this test, the Toxic threshold value was between 1.08 g/m³ and 10.8 g/m³ of the active compound I.3.

The results are shown in Table 3.

50

55

Table 3

Duration of the test in weeks	Concentration of the impregnating solution (%)	Quantity of active compound concentrate absorbed in g/m ³ wood			State of the larvae at the end of the test				
		min.	max.	M-value	dead	no wood digested	wood digested	living	not found
4	0.0144	82.08	116.64	103.97	27	3	0	0	
	0.0072	45.36	56.88	52.85	29	1	0	0	
	0.00144	10.08	11.23	10.80	4	6	1	1	(*1)
12	0.00144 (*2)	9.94	11.66	10.80	6	11	0	1	
	0.000144	0.55	1.21	1.08	4	12	11	3	
	0.0000144	0.09	0.12	0.11	1	4	23	2	
12	control samples	impregnated with chloroform			2	2	24	2	
		not treated			1	1	27	1	

Note:

(*1) One live larvae was found in the second specimen.

(*2) The remaining three specimens were tested for further eight weeks (12 weeks in total).

Comparative values of W. Metzner et al in "Holz als Roh- und Werkstoff, 35 (1977) 233-237", table 6 on page 236.

Table 4

Insecticide	toxic value (g/m ³)	Insecticide	toxic value (g/m ³)
DDT	5 - 10	Bassa (Baycarb)	17 - 30 - 44
Diazinon	12 - 18 - 32	Propoxur	18 - 30
Phoxim	7 - 12	Carbaryl	12 - 18
Chlorophoxim	12 - 20 - 32		

Example 11 Effectiveness against the termite species Reticulitermes santonensis

The toxicity against Reticulitermes santonensis of solutions containing the active compound I.3 in

chloroform having the concentrations mentioned in Example 10 was determined according to the detailed description of DIN EN 117 Edition 1981 which is concerned with the European standard method prescribed by the European Committee for standardization concerning wood preservatives, determination of the toxic value against *Reticulitermes santonesis*.

5 An outline of the method is as follows: (see DIN EN 117 for detail)

The same three wood-samples with impregnation treatment in vacuum as in Example 10 are provided.

They are exposed to 250 workers, 1 soldier and 1 nymph per batch for eight weeks, and afterward, the number of live/dead larvae is determined.

10 From this test, the toxic threshold value was between 0.135 g/m³ and 1.344 g/m³ of the active compound I.3.

The evaluation was made by the following standard:

*rating values:

0 = no attack

1 = attempted attack

15 2 = slight attack

3 = average attack

4 = strong attack

The results are shown in Table 5.

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Table 5

Concentration of protect agent tested in % (m/m)	No. of wood sample	Quantity of solution absorbed per wood sample in g/m ³	Quantity of protective agent absorbed per wood sample in g/m ³	average quantity absorbed in g/m ³	Results of evaluation			* rating
					surviving workers	Soldiers(S) or nymphs (N)		
1.44x10 ⁻⁵ %	1	17.75	0.136	0.135	55	S/N	4	
	2	17.47	0.134		51	S/N	4	
	3	17.69	0.136		58	S/N	4	
1.44x10 ⁻⁴ %	4	17.75	1.363		0	-	1	
	5	17.39	1.336	1.344	0	-	1	
	6	17.37	1.334		0	-	1	
1.44x10 ⁻³ %	7	17.54	13.471		0	-	1	
	8	17.56	13.486	13.463	0	-	1	
	9	17.49	13.432		0	-	1	
7.20x10 ⁻³ %	10	17.29	66.3936		0	-	0	
	11	18.03	69.2352	68.211	0	-	0	
	12	17.97	69.0048		0	-	0	
1.44x10 ⁻² %	13	17.79	136.627		0	-	0	
	14	17.72	136.090	136.627	0	-	0	
	15	17.86	137.165		0	-	0	
control samples diluent (chloroform)	16	17.72	0		50	-/N	4	
	17	18.15	0	0	57	S/N	4	
	18	17.77	0		48	S/N	4	
control samples untreated	19	0	0		55	S/N	4	
	20	0	0	0	62	S/N	4	
	21	0	0		64	-/N	4	

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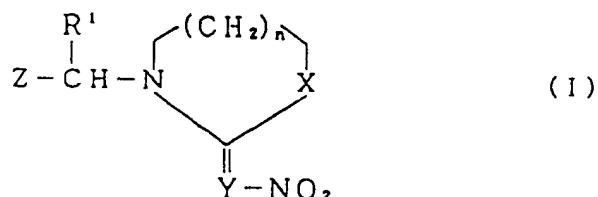
Comparative values of W. Metzner et al in "Holz als Roh- und Werkstoff," 35 (1977) 233-237, table 10 on page 236.

Table 6

Insecticide	toxic value g/m ³	Insecticide	toxic value g/m ³
DDT	> 1 500	Chlorophoxim	500
Dieldrin	50	Bassa	500
Lindan	75	Propoxur	140
Ethylparathion	200	Carbaryl	1 100
Phoxim	400		

Claims

15 1. Agents for preserving technical materials against insects, characterized in that they contain at least one compound of the formula (I)



wherein X is NH or S,
 Y is CH or N
 Z is 2-chloro-5-pyridyl or 2-chloro-5-thiazolyl,
 R¹ is hydrogen or methyl, and
 n is 0 or 1,

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2. Agents according to claim 1,
 wherein X is NH or S,
 Y is CH or N,
 Z is 2-chloro-5-pyridyl
 R¹ is hydrogen, and
 n is 0 or 1.

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3. Agents according to claim 1, wherein the active compound is selected from the group consisting of
 1-(6-chloro-3-pyridylmethyl)-2-nitromethyleneimidazolidine,
 3-(6-chloro-3-pyridylmethyl)-2-nitromethylenethiazolidine,
 1-(6-chloro-3-pyridylmethyl)-2-nitroiminoimidazolidine,
 1-(6-chloro-3-pyridylmethyl)-2-nitromethylenetetrahydropyrimidine, and
 3-(6-chloro-3-pyridylmethyl)-2-nitromethylenetetrahydro-2H-1,3-thiadine.

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4. Agents according to claim 1, wherein technical materials are wood or composite wood-materials.

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5. Agents according to claim 1, wherein insects are termites.

6. Process for preserving technical materials against insects, characterized in that the compounds of the formula (I) are allowed to act on said insects and/or their habitat.

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7. Use of the compounds of the formula (I) for preserving technical materials against insects.

8. Process for the preparation of agents for preserving technical materials against insects, characterized in that the compounds of the formula (I) are mixed with extenders and/or surface active agents.

9. Process for the preparation of agents for preserving technical materials against insects according to claim 8, characterized in that solvents and/or additional insecticides and/or fungicides are added.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 10 6384

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.5)						
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim							
X	EP-A-0 387 663 (BAYER) * Claims * ---	1-9	A 01 N 51/00 A 01 N 43/86 A 01 N 43/50 A 01 N 43/78 A 01 N 43/54 B 27 K 3/34						
D, X	EP-A-0 163 855 (NIHON TOKUSHU NOYAKU SEIZO) * Pages 47-48; example 7; page 50; example 50; claims * ---	1-9							
D, X	EP-A-0 192 060 (NIHON TOKUSHU NOYAKU SEIZO K.K.) * Page 111, lines 1-5; page 236; claim 4; examples 1,2; page 245; example 4 * ---	1-9							
X	EP-A-0 214 546 (NIHON TOKUSHU NOYAKU SEIZO) * Column 21, lines 45-51; claims * ---	1-9							
X	EP-A-0 256 407 (NIHON TOKUSHU NOYAKU) * Claims * -----	1-9							
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)						
			A 01 N B 27 K						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>15-07-1992</td> <td>DALKAFOUKI A.</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	15-07-1992	DALKAFOUKI A.
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THE HAGUE	15-07-1992	DALKAFOUKI A.							
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document							
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document									